AD NUMBER

AD-468 286

NEW LIMITATION CHANGE

TO

DISTRIBUTION STATEMENT - A

Approved for public release;
distribution is unlimited.

LIMITATION CODE: 1

FROM

DISTRIBUTION STATEMENT - B

Distribution authorized to U.S.
Gov't. agencies only.

LIMITATION CODE: 3

AUTHORITY

Cmdr., Picatinny Arsenal, Attn: Feltman Research Labs.,
Dover, New Jersey; Jul 15, 1969.

19990302125

SECURITY

MARKING

The classified or limited status of this report applies
to each page, unless otherwise marked.

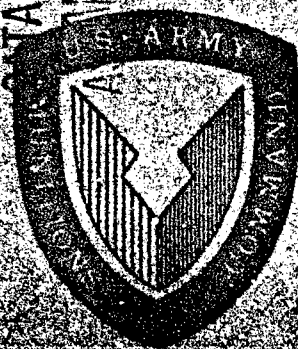Separate page printouts MUST be marked accordingly.

COPY NO. 35

TECHNICAL MEMORANDUM 1597

ON THE THEORY OF COMBUSTION
OF POWDER AND EXPLOSIVES

YA. B. ZEL'DOVICH

AUGUST 1965

PICATINNY ARSENAL
DOVER, NEW JERSEY

ON THE THEORY OF COMBUSTION OF
POWDER AND EXPLOSIVES

by

Ya. B. Zel'dovich

August 1965

ON THE THEORY OF COMBUSTION OF POWDERS AND EXPLOSIVES

Ya. B. Zel'dovich

1. INTRODUCTION

The extremely interesting work conducted in recent years by A. F. Belyayev in the laboratory of explosives, Institute of Chemical Physics, Academy of Sciences USSR, provides starting points for the theoretical investigation of a number of important problems, such as:

1) the problem of the space distribution of temperature and the state of matter in the combustion zone,

2) the problem of the combustion rate and its dependence on the conditions,

3) the problem of the conditions of transition of combustion into detonation,

4) the problem of the ignition of an explosive or powder and of the conditions necessary for its combustion.

As is well known, Belyayev [1] has cited convincing evidence of the fact that in the combustion of volatile secondary explosives, the explosive is first heated to the boiling point, then evaporated, and the vapors of the explosive enter into a chemical reaction after supplementary heating. By visual observation and photography, Belyayev demonstrated the presence of a dark zone between the surface of the liquid and the flame itself (the place where luminescence occurs, indicating an intense reaction). Thus, the theories that the combustion reaction occurs in the condensed phase or on the surface of separation of the liquid and gas under the action of the direct impact of the energy-rich molecules of the reaction products have been refuted. To a considerable degree the problem of the combustion of condensed explosive substances* has been reduced

---

*We shall henceforth use the abbreviation ES in place of "explosive substances."

1

to the theory of the propagation of a flame in gases, which was developed by D. A. Frank-Kamenetskiy and the author [2] simultaneously with Belyayev's first works on combustion. Inasmuch as combustion of the evaporated substance in the gaseous phase determines the observed combustion rate, the problem of the rate of steady-state combustion contained nothing new in comparison with the problem of the combustion rate of a gas. The specific features of the problem appeared in an analysis of the nonsteady-state phenomena and the conditions necessary for setting up steady-state combustion of a condensed substance, i.e. in the investigation of the limits of existence of the steady-state system. On the one hand, a chemical reaction in the condensed phase might be expected at a temperature approaching the boiling point; the rate of such a reaction can be substantial as a result of the great density of the condensed phase; the reaction rate also increases with increases in the boiling point, for example, with increasing pressure. The author has found an expression for the boundary above which the reaction in the condensed phase makes steady-state combustion impossible. The physical meaning of the boundary, however, did not become fully clear until later, after Belyayev [3] had shown that the boiling of a liquid ES greatly facilitates the appearance of detonation. It became clear that the chemical reaction in the liquid leads to its boiling and foaming, and, consequently, to detonation, and the expression found for the boundary of the possibility of steady-state combustion represents the condition of transition of combustion to detonation.

Another aspect we have investigated is related to the observation that an extremely great amount of heat is stored in the zone of heating of the condensed phase from the initial temperature to the temperature at which transition to the gaseous phase is accomplished (i.e. the boiling point). Changes in this heat reserve, which (the changes) are absent only in a strictly steady-state system, exert a very strong influence on the energy balance of combustion. The physical results go along two lines:

1) ignition of the ES and the realization of steady-state combustion require the creation of the indicated heat reserve; the principles of combustion theory are thus established;

2) it is found that a steady-state system of combustion becomes unstable under definite conditions; the heat reserve in the narrow zone of heating either is rapidly consumed by the accelerated (on account of this heat) flame, or is dissipated within the condensed phase with simultaneous deceleration of the flame; the end result of the deviation from a steady-state system in both cases is quenching of the ES. A supplementary condition, necessary for steady-state, stable combustion of a condensed substance, is formulated. Thus, a theory of a limit, beyond which quenching of combustion follows, is given.

Belyayev's experimental investigations pertained to liquid secondary explosives -- methyl nitrate, nitroglycol, nitroglycerin, and secondary explosives solid at room temperature, but melting upon ignition (TNT, picric acid, etc.).

We believe -- at present this is only a hypothesis -- that our theoretical investigations also pertain to the combustion of powders, and

primarily to smokeless powder. Classical internal ballistics does not touch on the problem of the intimate mechanism and stages of the chemical reactions that compose the essence of powder combustion. However, the whole series of Belyayev's arguments and our (D. A. Frank-Kamenetskiy and the author) work remain applicable. The hypothetical scheme of powder combustion currently proposed differs only in the fact that instead of reversible evaporation we should speak of a primary (irreversible) conversion of the powder to a gas; however, conversion does not yet occur to the final combustion products, which are followed in the gaseous phase by the reaction of "combustion itself," accompanied by the evolution of the bulk of the heat of the reaction.

The reader interested in the new physical concepts pertaining to powder combustion, the theory of ignition, and the combustion limit can without loss skip Part 3 (pp. 6-17), devoted to more formal problems, and Part 4 (pp. 17-21), in which the problem of the transition of combustion to detonation could not be brought up to a comparison with the experimental findings on account of the absence of much necessary information and data on the roles of other factors.

2. BASIC PREMISES OF THE THEORY OF STEADY-STATE COMBUSTION. SCHEME OF POWDER COMBUSTION

Let us recall and assemble here the basic premises of the theory of steady-state combustion, including those that are scattered in the literature cited above.

The initial state of the powder or ES has been set and quite accurately determined. Such a state -- composition and temperature -- of the combustion products can be determined under definite assumptions, for example, of the achievement of complete chemical equilibrium or of the fact that the reaction proceeds to definite chemical products (nitric oxide); the selection of the initial assumptions is controlled experimentally -- at least at present, in the absence of sufficient information on the kinetics of chemical reactions at high temperatures.

The temperature of the combustion products T_c is high as a rule -- 1200-2000°C, and the combustion products represent a mixture of gases. The entire temperature range from T_o to T_c is realized in the combustion zone; it is possible to show that under the conditions of a slow process of nonsteady-state combustion in comparison with the speed of sound, no break in the temperature can exist; all intermediate temperatures are realized. Simultaneously with a change in the temperature from T_o to T_c, a change in the aggregated state also occurs.

For the case of secondary ES capable of evaporation, as Belyayev indicates, the change in the aggregated state occurs at the boiling point corresponding to the external pressure. Actually, the rate of evaporation from the free surface of a superheated liquid is extremely great,* and

---

*The dependence of the evaporation rate on the superheating is easy to find by using the principle of detailed equilibrium. The coefficient

superheating of it is practically impossible. The dilution of the vapors by the reaction products, diffusing from the combustion zone, even somewhat reduces the temperature of the liquid surface in comparison with the boiling point.

More complex and less studied from the physicochemical viewpoint is the process of powder combustion. The vital influence of pressure on the combustion rate undoubtedly indicates a role of the gaseous phase. Letan and other researchers [10, 11] believe that the collision of molecules of the gaseous reaction products, which possess sufficient energy, produces the decomposition of the molecules of the powder components situated in the surface layer. Such a concept leads to proportionality of the combustion rate to the pressure and its dependence on the temperature of the combustion products.

The theory of the action of direct collision of gas molecules can also be called the temperature drop theories: they have meaning only in the case when there is a boundary between the cold powder and the hot reaction products; if the temperature of the powder and that of the gas are the same at the surface of separation, then activation as a result of thermal motion in the solid, and not activation by collision of the gas molecule, is far more probable.

In the presence of a temperature drop between the gas and the solid powder, a heat flux of enormous intensity, a hundred times exceeding the evolution of heat of combustion, should arise. Obviously, such a heat flux cannot exist during combustion.

We were forced to give up the naive molecular representations of direct collision and to seek another mechanism for powder combustion.

---

of accommodation, i.e. the probability of adhesion of vapor molecules striking the surface of a liquid, is assumed equal to 1. The number of molecules evaporating in a unit time is equal to the number of molecules incident on the surface in a unit time at the equilibrium pressure, which in turn is equal to the product of $\frac{1}{2}$ the number of molecules in a unit volume of the vapor n and the mean velocity of the molecules in the direction normal to the surface c_x.

If the superheating of the surface is such that the equilibrium vapor pressure with respect to $1 + \beta$ is greater than the external pressure, the rate of evaporation, expressed as the linear rate of outflux of vapor from the surface, comprises $\frac{1}{2}\beta c_x$. The rate of combustion in 1 mm/sec of liquid ES corresponds at atmospheric pressure to a rate of vapor outflux of the order of 50 cm/sec, to which β from 0.001 to 0.002 and a superheating of 0.02-0.04° correspond. At an accommodation coefficient $\alpha \neq 1$, and with all other conditions equal, the superheating increases in pro-

portion to $\frac{1}{\alpha}$. Finally, the superheating is proportional to the combustion rate.

Smokeless powder, which is based on polyatomic nitroesters of cellulose, cannot be distilled under normal conditions or under vacuum. When heated it decomposes, liberating a number of products, including the substances that are contained in the combustion products of the powder (carbon dioxide, carbon monoxide, water vapors, and partly nitric oxide). Can we not assume that a decomposition of this nature, accelerated by the temperature increase, also represents a combustion process, i.e. that combustion and conversion to a gas represent one inseparable step, or in another formulation -- that chemical reactions do not proceed in the gaseous phase -- chemical transformation proceeds only in the solid phase and upon transition of the solid phase to a gas?

The temperature of the combustion products is predetermined by the value of the heat of reaction. If the final reaction products are immediately liberated from the surface of the solid powder, no more chemical reactions and evolution of heat occur in the gaseous phase. Hence, the reaction products liberated from the powder, which possess a definite composition, should also have a final temperature T_c; the powder itself (solid phase) should also possess this same temperatures on the boundary where the gas is evolved, under the assumptions we have made.

This seems quite improbable, keeping in mind the extremely high temperature of powder combustion. The difference of the conditions during combustion from the usual thermal decomposition lies in the rapidity of the process: at a combustion rate of 1 mm/sec, the effective width of the heating zone is less than 0.2 mm, and the time of heating less than 0.2 sec (these values depend little on the temperature of the surface, of which we shall speak below.

In the case of such rapid heating, and energetic supply of heat, the increase in the temperature of the powder is limited only by the endothermic reactions, which are accompanied by its transition into the gaseous phase.* The rate of these reactions at low temperatures is less than the rate of normal decomposition, but as the temperature increases, the rate of the endothermic reactions rises more rapidly,** and at some temperature T_d reaches a value equal to the rate of combustion. This temperature will also be achieved on the surface of separation of the powder

_____

*The reaction does not have to be endothermic for the temperature of the solid powder not to reach the combustion temperature; it is necessary only that not all the heat of combustion be liberated in the reaction of gas formation, i.e. that the reaction be less exothermic than the combustion reaction. This determines the possibility of combustion, i.e. the subsequent reaction of the gases with evolution of heat. The reservation made here pertains to all cases, while we shall speak below simply of endothermic reaction.

**In connection with this, we should mention the enormous value of the preexponential factor in the expression for the probability of evaporation in the case of polyatomic molecules (see Langmuir [4]).

and gas.

The chemical energy of the final combustion products is less than the chemical energy of the powder: it is precisely in the liberation of the chemical energy and its conversion to thermal energy that the essence of combustion lies. The chemical energy of the gaseous products obtained in the endothermic decomposition of powder is obviously greater than the chemical energy of the powder. The products of such a decomposition react further, i.e. burn in the gaseous phase, liberating the bulk of the heat.

Thus, in our opinion, endothermic decomposition with the formation of energy-rich intermediate products is the analog of the evaporation of low-molecular ES in the combustion of powder. Let us note the features of the difference: evaporation occurs without the cleavage of chemical bonds; we might expect that the decomposition temperature of powder, T_d, will prove to be higher than the boiling points, T_b, of such substances as methyl nitrate (63°), nitroglycol (200°), nitroglycerin (250°) and TNT (300°). Evaporation is a reversible process, and T_b can be found by measuring the vapor pressure; T_b depends on the pressure at which the combustion occurs, but has practically no direct dependence on the combustion rate (see the footnote to p. 3). On the other hand, the decomposition temperature T_d is determined kinetically from the condition that the rate of decomposition is equal to the combustion rate; otherwise the front of the flame would approach the surface, the heat flux would be intensified, and the temperature of the surface T_d would increase until it would no longer correspond to the abovementioned condition. We might expect that the only factor determining T_d would be precisely the combustion rate; others, such as, for example, the pressure, initial temperature T_o, influence T_d only insofar as they change the combustion rate. However, the dependence of T_d on the combustion rate should also actually be weak. The decomposition rate is an exponential function of the temperature; the heat of activation, which includes the heat of reaction for the endothermic reaction, is great; under these conditions, a small change in T_d will be sufficient to produce a considerable change in the decomposition rate, i.e. to compensate for a substantial change in the combustion rate. We shall neglect the variation of T_d. Hence, in the future, wherever no special reservations are made, we shall treat the combustion of ES and powder together, denoting T_b as the temperature on the surface of separation of the condensed phase and the gas (the boiling point or, correspondingly, the decomposition temperature) and L as the thermal effect of transition from the condensed phase to the gaseous phase (the latent heat of evaporation or, correspondingly, the heat of decomposition).

3. MATHEMATICAL THEORY OF THE STEADY-STATE SYSTEM AND THE COMBUSTION RATE

Let us introduce a system of coordinates in which the flame is quiet. For definition, let us make the coordinate plane YOZ coincide with

6

the surface of separation of the condensed phase (abbreviated C phase) and the gas, where the C phase lies to the left when $x < 0$. In a system in which the flame is quiet, matter should be moved. The rate of motion of matter, u, has a positive sign. The rate of motion of the C phase far from the flame when $x < 0$ obviously coincides with the combustion rate u.

When x is increased, accompanied by heating, conversion to a gas, and chemical reaction of the matter, the rate of motion changes.

Let us begin by establishing the laws of conservation. For this purpose, let us set up a control surface 0 far from the flame; the values pertaining to this surface will be noted by the subscript "o," since they correspond to the initial state of the substance. All these gradients are also equal to zero at a sufficient distance from the flame, where we have placed the surface 0.

We can draw up the expressions for the laws of conservation at the place where we now select a second control surface, Π (we shall write the values pertaining to it without subscripts): here, in the steady-state system under consideration, the state of the matter between the control surfaces is constant; the amount of matter, energy reserve, and other quantities do not vary between the surfaces. The laws of conservation thus reduce to equality of the fluxes on the control surfaces.

The conservation of mass gives

$$\rho_0 u_0 = \rho u, \tag{3, 1}$$

where ρ is the density, u is the velocity.

The law of conservation can also be applied to each individual type of atom. Let us have g types of molecules (first subscript), consisting of f types of atoms (second subscript); let us characterize the composition of the molecules by the stoichiometric numbers ν_{il} (the number of atoms of the type l in a molecule of type i). The conservation of atoms of the given type l is written thus:

$$u_0 \Sigma c_{i0} \nu_{il} = u \Sigma c_i \nu_{il} + \Sigma \delta_i \nu_{il}. \tag{3, 2}$$

where c_i is the concentration of molecules of type i, c_{i_0} is the same on plane 0, δ_i is the diffusion flux of molecules of type i, Σ is the sign of summation over the index i from i = 1 to i = l.

Finally, the law of conservation of energy is written for the process proceeding at constant pressure, in the form:

$$\rho_0 u_0 H_0 = \rho u H - \eta \frac{dT}{dx} + \Sigma \delta_i h_i^0, \tag{3, 3}$$

where H is the specific enthalpy (heat content, H = E + pv), η is the

heat conduction, so that $-\eta \frac{dT}{dx}$ is the heat flux transferred by the molec-

ular heat conduction, h_i^0 are the values of the chemical energy of the

7

various molecules, i.e. their enthalpies h_i at absolute zero.* The values of h_i^0 and h_i satisfy the following equations:

$$h_i = h_i^0 + q_i = h_i^0 + \int_0^T c_p \, dT \tag{3, 4}$$

$$\rho H = \Sigma c_i h_i = \Sigma c_i h_i^0 + \Sigma c_i q_i = \Sigma c_i h_i^0 + \rho Q = \Sigma c_i h_i^0 + \rho \int c_p \, dT. \tag{3, 5}$$

Here we introduced not only the enthalpies H, h_i but also the thermal energy Q, q_i, the significance of which is clear from the formulas. The expression for the energy flux transferred by diffusion contains h_i^0, and not h_i because the transfer of physical heat was already considered in the heat conduction.

The expressions written are the most general; in particular, they hold true in the presence of a chemical reaction, since only the conversion of certain types of energy into others, certain types of molecules into others occur in a reaction, without any change in the amount of energy or the number of atoms.

Let us take the second control surface in such a way (position 1, subscript 1) that the chemical reaction can be neglected between 0 and 1. In this case the fluxes of individual types of molecules are also conserved, since in the gap under consideration, no conversion of some types of molecules into others occurs. In addition to the equations written above, we also have the following g equations:

$$u_0 c_{i0} = u_1 c_{i1} + i_{i1}. \tag{3, 6}$$

In particular, in the entire zone in which no chemical reaction occurs, the final reaction products (substances for which $c_{i0} = 0$) can be present, but their flux is equal to zero in the selected system of coordinates, in which the flame is quiet.

Thermal energy is conserved, since there is no conversion of chemical energy to thermal.

Using the notations introduced above, let us write the conservation of thermal energy in the following form:

$$\Sigma u_0 c_{i0} q_{i0} = \Sigma u_1 c_{i1} q_{i1} - \Sigma i_{i1} q_{i1} - \tau_1 \frac{dT_1}{dx}. \tag{3, 7}$$

---

*The heat content f of definite types of molecules containing all f types of atoms in various proportions should be taken as the zero heat contents for all g different types of molecules.

8

Using the preceding equations (3,6), we shall represent the law of conservation of heat in the following form:

$$\Sigma u_0 c_{i0} (q_{i1} - q_{i0}) = \eta \frac{dT}{dx}.$$

(3, 8)

Introducing the specific heat of the initial mixture

$$Q(T) = \frac{1}{\rho} c_{i0} q_i(T); \quad \frac{dQ(T)}{dT} = c_p.$$

(3, 9)

where c_p is the heat capacity of the initial substance, we obtain the equation

$$\rho_0 u_0 [Q(T_1) - Q(T_0)] = \rho u [Q(T_1) - Q(T_0)] = \eta \frac{dT_1}{dx}.$$

(3, 10)

By integrating this equation, we can easily find the temperature distribution in the preheating zone, where the reaction has not yet begun,

$$x = \frac{1}{\rho u} \int -\frac{\eta dT}{Q(T) - Q(T_0)} + \text{const}.$$

(3, 11)

Let us determine the value of the constant from the equation

$$T = T_k, \quad x = 0; \quad x_1 = \frac{1}{\rho u} \int_{T_k}^{T_1} \frac{\eta dT}{Q(T) - Q(T_0)}.$$

(3, 12)

This is the first concrete conclusion pertaining to the temperature distribution.

In the condensed phase we can assume with satisfactory accuracy:

$$\eta = \text{const}, \quad \rho = \text{const}, \quad u = \text{const}, \quad c_p = \text{const}, \quad Q = c_p T.$$

(3, 13)

In this case we find (the subscript 1 shows that the calculation pertains to the preheating zone, where the reaction has not yet begun)

$$x_1 = \frac{\eta}{c_p \rho u} \ln \frac{T_1 - T_0}{T_k - T_0} ; \quad T_1 = T_0 + (T_k - T_0) e^{\frac{c_p \rho u}{\eta} x}.$$

(3, 14)

Let us find the temperature distribution in the gas in the layers adjoining $x = 0$, in which the chemical reaction has not yet begun. The heat of evaporation or heat of endothermic reaction of gas formation L is equal to the drop of thermal energy of the starting material. Thus, when $x = 0$, there is a drop in the value of the heat flux on the phase boundary. Using one prime for the C phase and a double prime for the gas, let us

9

draw up the equation

$$x = 0, \; T_k = T' = T''; \; \tau_i'' \frac{dT''}{dx} = \tau_i' \frac{dT'}{dx} + \rho u L.$$ (3, 15)

Equation (3,10) remains in force.

Assuming constant η'' and c''_p in the gaseous phase (taking average values of these quantities, the product ρu is strictly constant everywhere), let us find the law of temperature distribution in the gas in the zone where the reaction is negligibly small.

Having performed the calculation, let us find a solution satisfying (3,10) and the boundary condition (3,15) in the following form:

$$T = T''_0 + (T_k - T''_0) \cdot e^{\frac{\rho u x}{\tau}} \; ; \; x \quad 0,$$ (3, 16)

where

$$T''_0 = T_k - \frac{c'_p (T_k - T_0) + L}{c''_p}.$$ (3, 16a)

T''_0 can be defined as the temperature at which the ES vapors would have an enthalpy equal to the enthalpy of the liquid ES at T_0, if the vapors did not condense when cooled and their heat capacity c''_p remained constant. The numerator of the fraction in expression (3,16a) represents the total expenditure of heat consumed for heating from T_0 to T_b and evaporation of a unit mass of ES.

Using (3,10), let us give an approximate estimate of the width of the zone l in the gas from the surface of the C phase $x = 0$ to the site of completion of the reaction. For a rough estimate, let us extrapolate the law (3,10) to $T = T_c$ and find the corresponding value of x.

We obtain:

$$l = \frac{\tau_i''}{c''_p \rho u} \ln \frac{T - T''_0}{T_k - T''_0} \simeq \frac{\tau_i''}{c''_p \rho u} \ln \frac{W + L}{L + c'_p (T_k - T_0)},$$ (3, 17)

where W is the heat of combustion.

As we shall see below, the chemical reaction proceeds almost entirely at a temperature close to the combustion temperature.

From this it follows: 1) that our estimate of the quantity l is numerically sufficiently close and 2) that the quantity l actually represents the width of the dark space between the surface of the C phase and the thin zone of intensive chemical reaction.

The expression for the diffusion flux, which we need to investigate the concentration distribution, has a complex form, since we are dealing with a polycomponent system in the presence of a temperature gradient. The diffusion flux of a given component depends in general not only on the concentration gradient of this component, but also on the concentration

10

gradients of the other components (an increase of some components by others)* and on the temperature gradient (thermal diffusion).

The simplest case represents a mixture of gases in which thermal diffusion and expansion are absent. In the presence of a temperature gradient, diffusion equilibrium in such a mixture is achieved at constancy of the partial pressures of each component.

It is obvious that constancy of the partial pressures should be required, and not of the concentrations, since the total pressure is preserved in the presence of a temperature gradient, while the sum of the concentrations varies in proportion to ρ, i.e. in proportion to $1/T$.

The diffusion flux is proportional to $\delta_i \sim \text{grad } p_i$; to bring the expression obtained into correspondence with the usual definition of the diffusion coefficient D, pertaining to the isothermal case, let us write for a flat flame

$$i_i = -D \frac{c_i}{p_i} \frac{dp_i}{dx} = -\frac{D}{T} \frac{d(c_i T)}{dx}. \qquad (3, 18$$

Then let us assume

$$D = \frac{\gamma_i}{c_p \rho} = \varkappa, \qquad (3, 19$$

where $\varkappa$ is the so-called thermal diffusivity.

We shall consider, finally, that the chemical reaction proceeds without a change in the number of molecules, without a change in the average molecular weight of the mixture (in essence, this is already necessary to have equality of the diffusion coefficients and their equality to the thermal diffusivity of the mixture).

In such a case the density of a mixture of gases is inversely proportional to the absolute temperature. We can rewrite the expression for the diffusion flux:

---

*In contrast to thermal diffusion, the increase in the value of the term that is given in the text has practically not been investigated. Its existence is easy to establish by a consideration of the three-component system A, B, C, in which the properties of A and B are extremely close, while C differs sharply from them. Let us place in contact mixture I: z parts of A and $(1 - z)$ parts of B, on the one hand, and II: z C and $(1 - z)$ B, on the other. If C is many times heavier than A and B, then A from the first mixture will diffuse into the second, displacing B -- up to a composition I: z A, $(1 - z)$ B and II: z C, $(1 - z)z$ A, $(1 - z)^2$ B. The concentration gradient of A produced a flux of B, the concentration of which was constant; only later does slow diffusion of C occur, as a result of which all the concentrations are evened out. The theory of the problem was recently discussed by Hellund [5].

$$\hat{z}_i = -\frac{D}{T}\frac{d(c_i T)}{dx} = -\varkappa\rho\frac{d(c_i/\rho)}{dx}.$$ (3, 20)

We can transform the basic equation of the law of conservation of energy, moreover, written in such a form that it is not violated even in the presence of a chemical reaction (3,3), for a gaseous mixture, using the assumptions we made about diffusion

$$\rho_0 u_0 H_0 = \rho u H - \eta\frac{dT}{dx} + \Sigma_i h^0_i = \rho u H - c_p \varkappa\frac{dT}{dx} - \varkappa\rho\Sigma h^0_i\frac{d(c_i/\rho)}{dx} =$$

$$= \rho u H - \rho\varkappa\left(\frac{dQ}{dx} + \frac{dH^0}{dx}\right) = \rho u H - \rho\varkappa\frac{dH}{dx}.$$ (3, 21)

Reducing by the quantity $\rho u = \rho_0 u_0$, we obtain the differential equation

$$\frac{\varkappa}{u}\frac{dH}{dx} = H - H_0.$$ (3, 22)

Its general solution has one arbitrary constant

$$\int\frac{dH}{H - H_0} = \int\frac{u}{\varkappa}dx + \text{const}; \quad H = H_0 + C\cdot e^{\int\frac{u}{\varkappa}dx}.$$ (3, 23)

The solution remains finite with unlimited increase in x if and only if C = 0, so that

$$H \equiv H_0.$$ (3, 24)

Thus, we have established that the specific (per unit mass) enthalpy is constant in the entire space occupied by the gaseous phase from x = 0 to $x \to \infty$; close to x = 0 the temperature, composition, and density of the gas vary rapidly on account of transfer processes and the chemical reaction; our result establishes a relationship between the changes in the temperature and composition in the gas. At the same time we elucidated the assumptions under with such a relationship holds true.

Let us recall that (3,24) was postulated without derivation by Lewis and Elbe [6] for gas combustion.

In the cited reference [2] similarity of the concentration fields (relative concentrations or partial pressures) and the temperature field was also established for gas combustion, from which constancy of the enthalpy in the entire combustion zone also follows.

Similarity was established in [2] by a consideration of the second order differential equations of diffusion and heat conduction. Under the assumptions made about the diffusion coefficient and heat conduction,

similarity of the fields -- and that means constancy of the enthalpy as well -- occurs in the entire space in the case of gas combustion, and, moreover, not only in the steady-state, but in any nonsteady-state problem. It is necessary only that there be no removal of heat by radiation or by heat-withdrawal to the walls of the vessel, for there to be no supplementary -- in addition to the chemical reaction -- sources of energy. These conditions also pertain to the combustion of powder or ES and were tacitly considered by us in writing the equations where the corresponding factors are absent.

In the case of combustion of a condensed substance, conservation of enthalpy and similarity occur only in the gaseous phase, only in part of the space. In the C phase the diffusion coefficient is much less than the thermal diffusivity coefficient; heating of the C phase occurs by heat conduction without dilution by diffusion; the enthalpy of the C phase on the boundary where $x \to 0$ (from the side $x < 0$) is greater than the enthalpy of the C phase far from the reaction zone and greater than the enthalpy of the combustion products. The advantage of the derivation cited here lies in the fact that constancy of the enthalpy in the gaseous phase and its equality to H_0 (H_0 is the enthalpy of the C phase far from the combustion zone, when $x \to -\infty$) were obtained regardless of the state of the intermediate layers of the C phase. We should emphasize especially that constancy of the enthalpy in the combustion zone occurs only for the steady-state process. The presence of layers of the C phase possessing increased enthalpy opens up the possibility in the nonsteady-state process of a temporary change in the enthalpy of the gas and the combustion temperature (for more discussion of this, see Part 5).

Let us find the concentration on the phase boundary when $x = 0$, $T = T_b$. Under the same assumptions that were made in deriving the constancy of the enthalpy, we find

$$p_{init} = \frac{T_\cdot - T_\kappa}{T_\cdot - T_0''} p = \frac{W - c'_p (T_\kappa - T_0)}{W + L} p. \tag{3, 25}$$

$$p_{fin} = \frac{T_\kappa - T''_0}{T_\cdot - T_0''} p = \frac{L + c'_p (T_\kappa - T_0)}{W + L} r. \tag{3, 26}$$

where p_{init} and p_{fin} are the partial pressures of the initial and final substances. Thus the evaporation of ES occurs in a medium of diluted vapors; the corresponding lowering of the surface temperature according to the Clausium-Clapeyron Law is

$$-\Delta T_k = \frac{RT_k^2}{L} \cdot \frac{\Delta p}{p} = \frac{RT_k^2}{L} \frac{L + c'_p (T_k - T_0)}{W + L}, \tag{3, 27}$$

this value, for example, for nitroglycol, reaches $9°$. Actually the combustion reaction is accompanied, as a rule, by an increase in the number of molecules, a drop in the average molecular weight, and the diffusion

13

c efficient of the vapors proves to be less than the thermal diffusivity of the mixture. We should think that the order of magnitude of ΔT_b would not change in this case.

The combustion rate enters into the equation as a parameter; in the most general case, set by an arbitrary value of the combustion rate, we can always perform a numerical integration of the system of ordinary second order differential equations, which are obeyed by the temperature distribution and the concentration distribution (the equations of the heat conduction and diffusion, all with a consideration of chemical reaction; argument -- coordinate). The integration is conveniently conducted from the side $x \gg 0$ of the final reaction products. At an arbitrary value of the rate, generally speaking, the boundary conditions will not be fulfilled when $x \ll 0$. It suffices us to perform the numerical integration to the place where the reaction rate can be neglected and it can be established whether the conditions (3,6), (3,7), (3,8) written above are fulfilled.

Performing the integration with various values of the parameter u, we find by trial and error a value at which the boundary conditions are satisfied, and this is the true value of the combustion rate.

We find the state of the reaction products at $x \gg 0$, from which we perform the integration, from the laws of conservation; these same laws are included in the differential equations. In the general case of different D and χ, there are no simple relationships between the concentrations and the temperature. However, the fluxes of molecules of various types and the heat flux are interrelated by equations (3,2) and (3,3). Hence the fulfillment of one of the conditions (3,6), (3,8) leads to the fact that the remainder identically prove to be fulfilled. By varying one quantity u, we should achieve fulfillment of one condition, which is always possible.

The method developed in [2] of integration of the equations of temperature and concentration distribution in the flame is based on the following idea: the rate of a chemical reaction increases unlimitedly with increasing temperature; in the presence of some temperature distribution, the reaction must always be considered at a temperature close to the maximum; as D. A. Frank-Kamenetskiy has shown in a work on thermal explosion [7], the rate constant of the reaction changes e times when the temperature changes by the quantity $\theta = \frac{RT^2}{E}$, where R is the gas constant,

E is the heat of activation. This temperature range is also a deciding factor; considering the interval θ small in comparison with the interval from T_c to T_0 (for this it is necessary that $E \gg RT_c$), we can neglect the change in the matter constants and the temperature in the reaction zone. The fluxes of heat and of the reacting components (but not the temperature and concentration) also change greatly -- the rate of change is proportional to the reaction rate. Under the assumption made, $\theta \ll T_c - T_0$, the equation looks like

$$-\frac{d}{dx} \chi \frac{dT}{dx} = -\chi \frac{d^2 T}{dx^2} = \phi, \qquad (3,\ 28)$$

14

where Φ is the volume rate of heat evolution in the reaction. Observing that when $T = T_c$, $\frac{dT}{dx} = 0$, we find

$$\frac{dT}{dx} = \sqrt{\frac{2}{\eta_1} \int_T^{T_c} \Phi dT}. \qquad (3, 29)$$

Let us write the condition of the heat balance, consisting of the fact that the entire amount of heat liberated in a unit time is generated by the chemical reaction

$$\rho u \, W = \int \Phi dx. \qquad (3, 30)$$

But with the aid of (3,29), we make the substitution

$$\int \Phi dx = -\eta_1 \frac{dT}{dx} = \sqrt{2\eta_1 \int \Phi dT}, \qquad (3, 31)$$

where the integral extends everywhere over the entire region in which $\Phi > 0$.

Finally

$$\rho_0 u_0 = \rho u = \frac{1}{W} \sqrt{2\eta_1 \int^{T_c} \Phi dT}. \qquad (3, 32)$$

The rate of evolution of heat depends not only on the temperature, but also on the concentrations of the reacting substances. In the case when $\chi = D$, the relationship of the concentrations to the temperature has been indicated above.

In the case $\chi \neq D$, as L. D. Landau has shown, the concentration of the initial substance in the reaction zone proves to be $\frac{\chi}{D}$ times greater than in the preceding case.

Let us write the approximate expression for the combustion rate, replacing

$$\int^{T_c} \Phi dT = \Phi_{max} \cdot \theta = \Phi_{max} \cdot \frac{RT^2}{E} \qquad (3, 33)$$

$$\rho_0 u_0 = \sqrt{\frac{2\eta \Phi_{max} RT^2}{W^2 E}}, \qquad (3, 34)$$

15

where Φ_{max} is the maximum value of the rate of heat evolution.

The integral (3,32) and approximate (3,34) formulas are more convenient for practical use than the closed expressions obtained after integration in the simplest cases.

The following basic conclusions are vital for a further development: the combustion rate is proportional to the square root of the reaction rate rate in the gas close to T_c. The combustion rate $\rho_0 u_0$* depends on the pressure as $p^{n/2}$, if the chemical reaction is first order, $\Phi \sim p^n$; the combustion rate depends on the temperature as $e^{-E/2RT}$, if E is the heat of activation of the reaction, $\Phi \sim e^{-E/RT}c$.

As can be seen from the preceding,** the combustion rate depends on the properties (T_c, η, Φ) of the combustion products and the layers lying closest to them; the combustion rate depends on the properties of the C phase insofar as the composition and temperature of the combustion products depend on the composition, heat value, and temperature of the C phase.

A formula for the velocity of the flame can also be obtained without integrating a second-order equation, essentially with an accuracy within a numerical factor of the order of 2. We shall proceed from the explicit equation (3,30), replace the integral by the product $\Phi_{max}\Delta x_{eff}$, and evaluate the effective width of the reaction zone Δx_{eff}, knowing the temperature interval and the order of magnitude of the temperature gradient

$$\Delta x_{eff} = \int_{\theta}^{\theta} \frac{dT}{dx} = \frac{\eta \theta}{\tau_i \frac{dT}{dx}} = \frac{\eta^{h}}{\rho_0 u_0 W}. \qquad (3, 35)$$

Combining these estimates, we obtain an expression differing from (3,34) only by the absence of the numerical factor.

The considerations on the velocity of the flame in gases pertain also to ES and powders; see also [8].

As applied to the combustion of nitroglycol, the velocity of the flame has been shown by A. F. Belyayev [9] to follow an exact exponential dependence on the temperature of combustion. For powders, the empirical formulas proposed by Muraour [10] and Jamaga [11] are already available in the literature. The content of these formulas reduces to the fact that the flame velocity depends on the combustion temperature of the powder; the very type of the dependence, according to Jamaga, is Arrhenius, just as it follows from the theory developed here. Muraour proposes a dependence of the form $u = e^{A+BT}$. As Frank-Kamenetskiy has shown [7], such a dependence is a good approximation to Arrhenius. Let us mention that both authors (Jamaga and Muraour) relate the velocity to the combustion

---

*ρ_0 -- density of the C phase -- practically constant.
**See especially the description of the general method for finding the rate by numerical integration.

16

temperature in a closed volume, calculated from the condition of equality of the energy of the powder at T_0 and the energy of the powder gases.

By analogy with gaseous systems, we shall call the combustion temperature in a closed volume $T_{explosion}$, leaving the notation T_c for the combustion temperature at constant pressure.

Actually the combustion products, just formed and situated at the very surface of the powder, always possess the combustion temperature at constant pressure, calculated from the condition of equality of the enthalpy of the powder at T_0 and the enthalpy of the products at T_c.

In the case of the process in a closed volume, the combustion products that had appeared earlier also had this same temperature T_c; however, after this, the temperature of the gases increased as a result of adiabatic compression during the increase in pressure during combustion. Thus $T_{explosion}$ is actually realized only as an average value -- cf. Mache's theory of the explosion of a gaseous mixture in a closed volume [12].

The combustion rate actually depends on T_c. Fortunately, the relationship of the two temperatures is elementary:

$$T_{explosion}:T_c = c_p:c_v$$

and conversion from one to the other does not change the form of Jamaga's and Muraour's formulas. These formulas, pertaining to the combustion rate at a high pressure, of the order of 1000 kg/cm^2, are in poor agreement with one another. The most probable value of the heat of activation of the reaction, following from the formulas, is 24 kcal/mole.

There are many works on the dependence of the rate of powder combustion on the pressure, enumerated in all courses on internal ballistics. Various authors give relationships from $u \sim p^{0.5}$ to $u \sim p^1$, which corresponds to reaction orders from first to second. In the case of powder there is a complicating circumstance: at low pressure the combustion products contain a substantial amount of nitric oxide, which disappears at high pressure. Thus it is possible that a change in the pressure influences the velocity of the flame, also on account of the change in the direction of the reaction and the combustion temperature. At present it does not seem possible to quantitatively distinguish these factors.

4. REACTION IN THE LIQUID PHASE AND TRANSITION OF COMBUSTION TO DETONATION*

Let us preface our exposition of the problems posed in the heading by a finer analysis of the theoretical fundamentals.

We have asserted above that the reaction proceeds basically at a temperature close to the combustion temperature.

Actually, the reaction rate reaches a maximum close to the combustion temperature. The fact that this region is decisive is detected best

---

*The material following pertains to the combustion of liquid secondary ES.

17

of all when we attempt to calculate the combustion rate .. ' ie assumption
of a reaction proceeding, for example, to an extent of :0%, with a corres-
pondingly reduced thermal effect and combustion tempera: .: the rate
proves to be less than the true rate. We might describe the matter in such
a way that combustion at a temperature close to T_c is propagated most rap-
idly and is responsible for a greater flame velocity, at which the reaction
cannot proceed at any lower temperature, although the absolute value of the
rate at this lower temperature may be substantial.*

In the case of gas combustion, such a premise is a rule, exceptions
from which are extremely rare.

In the case of combustion of a liquid ES, a change in the aggregated
state causes a sharp change in the properties at constant temperature.
The volume rate of liberation of heat in the gas falls monotonously as the
temperature is lowered, beginning with a temperature close to T_b. At T_b,
with transition from gas to liquid, the volume rate of heat liberation in-
creases sharply, jumpwise, on account of a sharp increase in the density.
As the temperature is further lowered, the density of the liquid remains
constant, and the volume rate of heat evolution again drops according to
the Arrhenius law of the temperature dependence of the reaction rate.

The width of the reacting layer also increases jumpwise as a result
of the increase in heat conduction when the vapor is converted to a liquid.

In the gas the combustion rate decreases with decreases of the com-
bustion temperature -- if a lowered combustion temperature with a given
initial state is obtained as a result of incomplete combustion. The rate
of combustion again rises, however, when the combustion temperature does
not exceed T_b, so that the reaction is limited by the liquid phase; the
causes of the increase are indicated above. On the other hand, here it is
better to speak not of the combustion rate, but of the rate of propagation
of the wave of heating of the liquid on account of the reaction in the
liquid phase. The maximum temperature achievable in the liquid is limited
by the quantity T_b, just as the combustion temperature, properly speaking,
is limited by the quantity T_c. The calculation of the velocity of the
heating wave in the liquid presents no difficulties [see formulas (3,32),
(3,34)] if the kinetics of the chemical reaction in the liquid phase is
known.

If the velocity of the heating wave calculated in this way is less
than the combustion rate, then the reaction in the liquid phase does not
disturb the steady-state character of the combustion, but only negligibly
changes the temperature distribution in the liquid.

On the other hand, if the velocity of the heating wave is greater
than the combustion rate, a steady-state system is impossible: actually,
during combustion the liquid surface is heated to the temperature T_b;
however, at this temperature a chemical reaction begins to proceed in the
liquid, heating the adjoining layers of liquid before they can evaporate

---

*The explanation was first advanced by the author in a discussion
at the Scientific Council of the Institute of Chemical Physics in 1940.

and burn. The temperature distribution in the liquid proves to be non-steady-state.

What actually occurs in this case? The heating wave will travel out beyond the surface on which the combustion of the gas evaporates the liquid. An expanding region of liquid, brought up to the temperature T_b, but not yet evaporated, is formed in the temperature distribution.

At the temperature T_b the reaction in the liquid phase is not entirely arrested; the increase in the temperature of the liquid is arrested at T_b, and the cause of the stoppage lies in the fact that a further supply of heat leads to evaporation of the liquid. At the free surface of the liquid, evaporation proceeds without lag and superheating and removes heat from the closest superheated layers. However, as the wave of heating up to T_b moves forward, and the region of liquid heated to T_b expands, in this region the liquid becomes superheated as a result of the chemical reaction and boiling occurs.

Belyayev [3] has shown experimentally that a boiling ES detonates when ignited.* The explanation he advanced is quite satisfactory: on the one hand, boiling sharply increases the surface of liquid-vapor separation on which combustion occurs and thus increases the amount of the ES burned in a unit time, increasing the mechanical effects (increase in pressure) accompanying combustion. On the other hand, the presence of bubbles in the liquid also extremely greatly increases the combustibility of the system and its sensitivity to mechanical influences.**

Thus we can predict that an excess of the velocity of the heating wave over the combustion rate will lead to a transition of combustion to detonation.

The condition of transition of combustion to detonation can be pre-calculated according to the experimental data with minimal values of the reaction mechanism: in this calculation we shall use: 1) the dependence of the combustion rate on the pressure, measured experimentally, $u = u_1 p^m$; 2) the rate of heat evolution Φ_{liq} during the reaction in the liquid phase; this quantity can be found calorimetrically, or calculated from the reaction rate, measured according to the rate of gas evolution; let us represent the temperature dependence of the rate of heat evolution in the form:

$$\Phi_{\varkappa}' = A e^{-F'RT}; \qquad (4,\ 1)$$

3) the physical constants of the liquid: heat conduction η', heat capacity c_p', density ρ', and heat of evaporation L; the last can be found

---

*Unfortunately, for procedural reasons, the experiments were conducted with an extremely small amount of liquid, part of which evaporated. A more detailed investigation would be extremely desirable.

**In an unpublished work of 1939, Yu. B. Khariton observed a strong drop in the sensitivity to shock of liquid ES when it was freed from bubbles.

according to the dependence of the vapor pressure on the temperature

$$p = Be^{-L/RT}. \tag{4, 2}$$

Let us draw up an expression for the rate of propagation of the heating wave: the reaction proceeds only so far as to heat the ES from T_o to T_b, so that we should substitute the thermal effect $W' = c_p'(T_b - T_o)$ into formula (3,32). This thermal effect comprises only a small portion of the thermal effect of the reaction that goes to completion; hence the change in concentration of the reacting molecules can be neglected.*

The expression for the velocity u' of the heating wave takes the form:

$$u_1' = \frac{1}{\rho' W''} \sqrt{2\tau_i' \Phi'(T_i)u'} = \frac{1}{\rho' c_p'(T_i - T_0)} \sqrt{2\tau_i' \cdot A e^{-E'/RT_i} \cdot \frac{RT_i^2}{E'}}. \tag{4, 3}$$

e+ find the dependence of the velocity u' on the pressure: the pressure does not enter directly into the last formula; however, the surface temperature T_b depends on the pressure.

Comparing (4,3) and (4,2), we find

$$u' = u_1' p^{E/2L}, \tag{4, 4}$$

where u_1' was calculated according to (4,3) for T_{b1} — the boiling point at a pressure of 1 atm; we neglected any other dependence of u' on T_b other than exponential. The value of the power $E'/2L$ is greater than one: thus, when the pressure is increased, the velocity of the heating wave increases more rapidly than the combustion rate; an increase in the pressure promotes a transition of combustion to detonation — in agreement with the experimental data. Let us find the condition of transition in the form

$$u' = u; \quad u_1 p^m = u_1' p^{E/2L}; \quad p = \left(\frac{u_1}{u_1'}\right)^{\frac{2L}{E - 2L m}}. \tag{4, 5}$$

We should mention that the use of the simple relationship (4,2) with constant L is possible only when $p \ll p_{crit}$. If the pressure obtained according to formulas (4,5), (4,6) becomes comparable with p_{crit}, a refined curve of the vapor pressure must be used in the calculation. As is well known, the heat of evaporation is lowered when the temperature is raised; formulas (4,4), (4,5) with constant L, measured at low temperature, give a high limiting value. Finally, if the pressure found exceeds the

_____

*Only if the products exert no sharp — positive or negative — catalytic influence on the reaction rate.

**Measured for the reaction in the gaseous phase.

critical pressure, above which transition of the liquid to the gas occurs continuously, then the theory developed here is inapplicable.

At present, with the scanty experimental material available, it would be premature to consider the problems of superheating of the liquid and the evolution of gaseous reaction products in the form of bubbles.

Let us mention in conclusion one principal factor: Belyayev's initial argument consists of a comparison of the probability of reaction and the probability of evaporation of a molecule of ES found in the liquid. From the fact that the heat of activation of the reaction can be greater than the heat of evaporation, he concludes that the probability of evaporation sharply exceeds the probability of reaction; hence, when heat is supplied, evaporation occurs and the reaction proceeds only in the gaseous phase. Does not a consideration of the reaction in the condensed phase contradict this basic premise? Actually, the argument cited is inapplicable without reservations. The probability of evaporation of an individual molecule cannot be written simply as $\nu e^{-L/RT}$, where ν is any frequency; in this form the formula is suitable only for molecules lying in the surface monomolecular layer, and, moreover, if we digress from condensation.

For molecules found within the liquid, the probability of evaporation is strictly equal to zero at all temperatures below the boiling point corresponding to the external pressure. And yet, the probability of reaction under these conditions, although small, is finite.* Only later, at a temperature exceeding the boiling point, does the probability of evaporation become appreciable, increase vigorously, and soon sharply exceed the probability of reaction. It is precisely this that Belyayev observed [13] in experiments on the ignition of nitroesters by combustion of a wire in which the rapid delivery of heat at atmospheric pressure led to evaporation, and not to its inflammation or detonation.

5. ON NONSTEADY-STATE COMBUSTION

It is impossible to consider in general form the differential equations of the heat conduction and diffusion in a medium in which a chemical reaction proceeds in addition, discarding the assumption of steady-state propagation of the system at a constant rate.

Below we: 1) shall neglect the chemical reaction proceeding in the C phase, 2) shall consider the surface temperature T_b as constant, and

---

*Belyayev considered this problem in his unpublished calculations and showed that for atmospheric pressure and low-boiling ES, the number of molecules evaporating in the surface layer is greater than the number of molecules reacting in a layer 1 cm thick, i.e. the ratio of the probability of evaporation to the probability of reaction is greater than the ratio of the number of molecules in a layer 1 cm thick to the number of molecules in the surface layer. However, the situation is changed under conditions approaching the transition of combustion to detonation at high pressure.

3) shall consider the relaxation time of the processes occurring in the gas as extremely small in comparison with the relaxation time (time of change) of the distribution of heat in the C phase. Limiting ourselves to a consideration of the periods of time considerable in comparison with the relaxation time of the processes in the gas, we shall consider that the state of the layer of gas closest to the surface, in which the chemical reaction is concentrated, corresponds at each moment to the distribution of heat in the C phase. After such a correspondence has been established, the problem reduces to a consideration of a comparatively slow change of the distribution of heat in the C phase.

In substantiation of point 2, let us mention that in the case of reversible evaporation (secondary ES), T_b depends practically not at all on the rate of evaporation and is only a weakly logarithmic function of the pressure; in the case of irreversible gas production (powder), T_b does not depend directly on the pressure and is only a weakly logarithmic function of the rate of gas formation.

In substantiation of point 3, let us cite some characteristic figures: let us define the relaxation time of the process in the gas as the ratio of the width of the zone of temperature change to the rate of motion of the gas.

In other words, we shall define the relaxation time as the time during which a definite particle of the gas travels over a path from the surface of separation to the place where the reaction is completed.

Let us analogously define the relaxation time of the distribution of heat in the C phase. Let us cite a numerical example pertaining to the combustion of powder at atmospheric pressure.

The density of the powder is equal to 1.6, combustion rate 0.04 cm/sec. The heat conduction of the powder is $5.1 \cdot 10^{-4}$ cal/cm·sec·°C, the heat capacity 0.36 cal/gram·°C, $\varkappa = 1 \cdot 10^{-3}$ cm^2/sec; if the distance $\varkappa/u$ at which the initial heating changes e times is arbitrarily called the

width of the zone, we obtain $\frac{\varkappa}{u} = 0.025$ cm, and the combustion time of such

a layer $\tau' = \frac{0.025}{0.04} = 0.625$ sec.

We shall also perform an analogous estimation for the gas. In the gas the velocity u is substantially greater, corresponding to a 10,000-fold drop in the density. The order of magnitude of the relaxation time in the

gas is equal to $\tau'' = 9 \cdot 10^{-5}$ sec, $\frac{\tau'}{\tau''} = 6,800$ times smaller than the relaxa-

tion time of the temperature distribution in the solid powder. When the

pressure is increased, the ratio $\frac{\tau'}{\tau''}$ decreases somewhat; at 100 kg/cm^2 it

is still equal to 75. These figures justify the method of consideration adopted in point 3.

Since the relaxation time of combustion in the gas is very small,

22

we have the right to consider that combustion in the gas is determined at each moment by the thermal state of the thin layer of the C phase closest to the surface of separation: the temperature distribution in the deeper-lying layers exerts no direct influence on the process occurring at the surface. The conditions in the gas should be determined entirely by the instantaneous value of the surface temperature and temperature gradient in the C phase near the surface; for the latter, let us introduce the abbreviated notation

$$\left(\frac{dT}{dx}\right)_{x \to 0} = \varphi. \tag{5, 1}$$

Let us consider the surface temperature (see above) T_b as constant.

The basic quantity characterizing combustion in the gas is the combustion temperature T_c. Let us find it by compiling the heat balance, related to a unit time. Heated to T_b, the C phase burns, giving gaseous combustion products, heated to T_c; the difference in the heat contents of the second expenditures comprises an amount of heat increased by the heat conduction within the C phase

$$\rho' u' \left[H'(T_k) - H''(T_i) \right] = \eta' \varphi. \tag{5, 2}$$

We can equip the product $\rho' u$ equally with a double prime (sign of the gaseous phase) and with one prime (sign of the C phase), since it is conserved. We selected the C phase for the sake of definition. Let us compare expression (5,2) with the elementary expression determining the combustion temperature in the steady-state system T_{sc}

$$H'(T_0) = H''(T_{sc}). \tag{5, 3}$$

Let us use the relationship between the heat content, heat capacity, and temperature, and obtain after simple transformations

$$T_c - T_{sc} = \frac{c'_p}{c''_p} \left[(T_k - T_0) - \frac{\eta'}{c_p' \rho' u'} \varphi \right]. \tag{5, 4}$$

In a steady-state system of combustion, the relationship between the quantities is such that the expression in brackets is equal to zero, and, just as we should have expected, the temperature T_c does not differ from T_{sc}, calculated according to (5,3).

In a steady-state system, moreover, the C phase, heated from T_0 to T_b, actually burns; however, the corresponding gain of energy is compensated for by a removal of heat into the C phase. Exact compensation is natural, since the heat withdrawn is used immediately to heat the C phase from the initial temperature T_0 to T_b.

Using the function

$$(T_k - T_0) \cdot \frac{\tau_i'}{c_p' \gamma' u_c'} \cdot \gamma_c = 0 \qquad\qquad (5,\ 5)$$

(the subscript "s" denotes steady-state), let us rewrite (5,4) in the form:

$$T_c - T_{sc} = \Delta \left(1 - \frac{\varphi}{\varphi_c} \frac{u_c'}{u'} \right); \Delta = \frac{c_p'}{c_p} (T_k - T_0). \qquad (5,\ 6)$$

The difference of the combustion temperature from its steady-state value depends not only on the value of φ (i.e. on the initial heating of the C phase), but also on the combustion rate u^2. In turn, the combustion rate u' depends on the combustion temperature

$$u' = Ae^{-FRT} . \qquad\qquad (5,\ 7)$$

At the given value of the temperature gradient φ, we have two equations for determining two quantities, u' and T_c. Let us investigate this system of equations by constructing curves in the system of coordinates u', T_c.

In Fig. 1 the thick line gives the curve corresponding to formula (5,7). Formula (5,6) contains φ as a parameter; the family of this lines corresponds to different values of φ; the direction of increasing φ is shown by an arrow. The thin lines represent a family of equilateral hyperbolae with common asymptotes: the Y-axis u' = 0 and a line parallel to the X-axis, $T_c = T_{sc} + \Delta$.
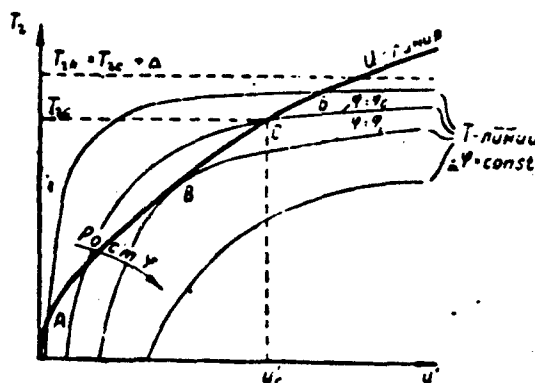

Fig. 1.

We shall call the thick line the U-curve, since it gives the dependence of the combustion rate on the temperature; let us call the thin

lines the T-lines, since formula (5,6) describes the dependence of the temperature on the combustion rate. In the natural sciences the concepts "a depends on b" and "b depends on a" are nonequivalent, while in mathematics $a = f_1(b); b = f_2(a); f_3(a,b) = 0$ have a quite identical meaning.

At large values of φ the curves do not intersect at all. Powder insufficiently preheated from the surface does not burn. With preheating and the inward propagation of heat, the gradient φ drops.

We finally reach the T-lines tangent to the U-curve at the point B at the value $\varphi = \varphi_B$. Beginning with this value of φ, the system of equations has solutions; combustion is possible. The critical value of φ_B corresponding to tangency determines the condition of ignition of the C phase and makes it possible to calculate the necessary amount of heat and the rate of heating. A calculation of φ_B will be presented below.

At still smaller values of φ, the curves, as is easily determined, always have two points of intersection each: this follows from the presence in curve (5,6) of a horizontal assymptote, and from the fact that at small T_c the exponential function (5,7) drops more rapidly than the algebraic curve (5,6), which has a vertical assymptote in common with the exponential function, $u' = 0$.

In particular, when $\varphi = \varphi_s$, we have beforehand a solution describing steady-state combustion: the equations are obviously satisfied by the solution $\varphi = \varphi_s$, $T_c = T_{sc}$, $u' = u_s'$ (point C, Fig. 1).

Let us write the value of φ_s

$$\varphi_c = \frac{c_p' \rho'}{\eta'} (T_k - T_0) u_c' \qquad (5, 8a)$$

(cf. 5,8b below).

As T_b changes to T_0 and below, the quantity φ_s first increases on account of the increase in the quantity $T_b - T_0$; soon, however, the exponential drop in u_s' reinforces the growth of $(T_b - T_0)$. As T_0 changes, the quantity φ_s passes through a maximum, $\varphi_{smax} = \varphi_B$. Consequently, one value of φ_s corresponds to two different steady-state systems, with two different T_0 and two different u_s'. Thus, we obtain a confirmation of the fact that two values of u' and T_c correspond to one value of the gradient. Each of them, at the corresponding value of T_0, describes a system satisfying the equations of steady-state combustion.

However, we have already established that the system of combustion in the gaseous phase should be determined by the value of φ, independent of the temperature distribution in the C phase at a great depth and, in particular, independent of T_0.

Let us compare the behavior of two possible systems, A and B, corresponding to the same φ. Let us imagine that system A is set up. A small drop in the combustion rate u', according to the T-curve, causes a drop in the temperature; the drop in rate corresponding (U-curve) to the temperature drop will be still greater, etc.; continuation brings us to an unlimited temperature drop, signifying quenching. If, on the other hand, proceeding from A, we somewhat increase the temperature or combustion

25

rate, then the same sequence of considerations leads us to the state of point B. On the other hand, the character of the intersection of the T- and U-curves that we have at point B (and at all points above B) guarantees stability; for example, when the rate is increased, the temperature rises weakly, the corresponding increase in the rate is small (less than the initial), etc.; the sequence reduces, reversibly, to B.

Thus, at a given φ, of two possible systems of gas combustion, the one that corresponds to a higher combustion rate and a higher combustion temperature is always set up.

We established above a method of finding the system of combustion, i.e. u' and T_c, rapidly established in the gaseous phase at a given state of the C phase (i.e. at given T_b and φ). In turn, the temperature distribution in the C phase also varies slowly as a function of the combustion rate. The distribution and gradient φ at each given moment depend on all the previous values of the combustion rate, on the entire thermal prehistory of the powder. This dependence is determined by the solution of the heat conduction equation with a set value of $T = T_b$ on the line $X(t)$, where $\dfrac{dX}{dt} = u'$.* This dependence cannot be calculated analytically. From equation (3,8) we find elementarily the limiting value of φ for prolonged maintenance of a constant value of u'

$$\lim \varphi = \frac{c_p' \gamma'}{\tau_i} (T_i - T_n) u'. \tag{5, 8b}$$

We are easily convinced that point C (Fig. 1) is stable with respect to slow changes in the temperature distribution in the C phase. Let there be point B, $\varphi < \varphi_s$, $u' > u_s'$. In a steady-state system, a greater value of φ corresponds to a large value of u'. Hence, there will be an increase in φ, accompanied by passage from one T-curve to another in the direction indicated by the arrow. The point of intersection of the T-curve and the U-curve is displaced in this case from B to C. At C the movement stops, since here not only does the system of combustion correspond to the thermal state of the C phase, but the state of the C phase also corresponds to the combustion rate. The establishment of steady-state combustion after ignition can be considered by the same method; its establishment is described on the graph as a rise from B to C.

We have tacitly assumed that point C, which describes the steady-state system, lies above the point of intersection B, as is shown in the figure.

Actually, the opposite case is also possible, where the point C lies below B, so that intersection of the U- and T-lines at point C occurs according to the type of point A (Fig. 2).**

---

*Here X is a coordinate perpendicular to the flame with respect to which the C phase is quiet.

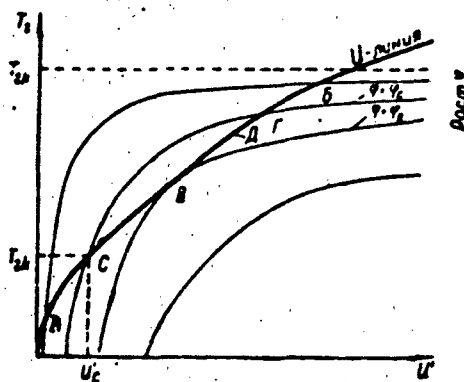**Let us mention that C describes a steady-state system at a given T_o.

Fig. 2.

What behavior of the system do we expect in this case? Let us imagine that the conditions of steady-state combustion are set up, and, primarily, the corresponding gradient φ_s. As we have seen, in this case, instead of C, another system Γ, with the same $\varphi = \varphi_s$, but a greater combustion rate, will very rapidly -- in a small relaxation time of the gas -- be established. A slow increase in φ, accompanied by movement of the depicting point from Γ to B, corresponds to the increased combustion rate.

Let us demonstrate for an arbitrary point D, lying on the segment B, that an increase in φ will occur in the case of Fig. 2.

φ_A is steady-state at $u_A{}'$ and corresponds to T_{OA}, which is higher than T_O, to which point C corresponds; that $T_O < T_{OA}$ can be seen from the fact that C lies below A at smaller T_c. If the identity (cf. 5,8a,6)

$$\varphi_A = \frac{c_P' \rho'}{\tau_i'}\,(T_A - T_{0A})\,u_A',$$

is fulfilled, then for the same rate and the T_O under consideration, the value that φ approaches,

$$\lim \varphi = \frac{c_P' \rho'}{\tau_i'}\,(T_A - T_0)\,u_A' > \frac{c_P' \rho'}{\tau_i'}\,(T_A - T_{0A})\,u_A' = \varphi_A \quad \Big\}$$
$$\lim \varphi > \varphi_A. \qquad \qquad \Big\}$$

The proof of the increase in φ remains in force for the edge of the segment at point B as well.

Thus, the increase in φ does not cease at B.

However, further increase in φ leads us to a T-line that does not intersect the U-curve, and combustion ceases.

The physical processes that occur in this case are the following:

the C phase, heated by an external source, begins to burn, but it burns at a rate exceeding the steady-state rate, and with a temperature of the combustion products exceeding the calculated theoretical temperature. Such intensive combustion occurs on account of irreversible expenditure of the amount of heat stored during ignition. After this reserve is exhausted, removal of heat into the C phase reaches such a great value that the flame is quenched. Thus, in the case of ignition, in place of steady-state combustion, we obtain an individual flash, rather energetic, but ending in quenching.

Steady-state combustion, possible in the sense that a system can be constructed satisfying the equations of steady-state combustion, essentially proves to be unrealizable as a result of its instability, described in detail above.

Let us determine the conditions, depending on which, one case or another occurs, and point C proves to be higher or lower than B.

At constant chemical composition and constant pressure, the initial temperature of the C phase T_o will vary.

In the initial form (5,2) we see that the family of T-lines (in which each curve corresponds to a definite value of φ) does not depend on T_o; (5,2) can be rewritten in the form

$$T_r = T_{ck} - \frac{\eta}{\rho' c_p'} \frac{\varphi}{u'}, \quad \text{где } H''(T_{ck}) = H'(T_k),$$

(5, 9)

so that T_{cb} is the theoretical combustion temperature of the C phase, heated to the highest temperature T_b.*

Hence, the same diagram with one U-curve and family of T-lines is suitable for all values of T_o. Only the position of the point C, which always lies on the U-curve, varies as a function of T_o. The relationship of T_{cb} to T_o is elementary. Steady-state combustion is possible only at T_o such that $T_{cb} > T_B$ is greater than the temperature corresponding to the point of tangency. Powder or secondary ES, cooled to a lower temperature, is incapable of steady-state combustion, and gives only flashes when ignited, as described above. Let us start on a calculation of the coordinates of point B, at which tangency of the T- and U-lines occurs.

The condition of tangency is formulated thus:

---

*Comparing (5,9) with (5.6) we obtain the identity

$$T_{ic} + \lambda = T_{ic} + \frac{c_p'}{c_p''}(T_k - T_0) = T_{ik} = \text{const.}$$

(5, 9a)

$$\lambda \cdot u'_c \varphi_r - 1 = \frac{c_p'}{c_p''}(T_k - T_0) u'_c \left[\frac{c_p' \rho'}{\eta'}(T_k - T_0) \cdot u'_c \right]^{-1} = \frac{\eta'}{\eta' c_p'} = x = \text{const.}$$

(5, 9b)

28

$$\left(\frac{dT_t}{du^*}\right)_U = \left(\frac{dT_:}{du'}\right)_{r..} \qquad (5,\ 10)$$

The left-hand derivative is taken along the U-line, the right -- along the T-line, at constant φ. Let us calculate these quantities. Let us use (5,7) and (5,9)

$$\left(\frac{dT_:}{du'}\right)_U = \left(\frac{du'}{dT_:}\right)_U^{-1} = \left(\frac{E}{2RT_:^2}\cdot u'\right)^{-1} = \frac{2RT_:^2}{E}\cdot\frac{1}{u'}; \qquad (5,\ 11)$$

$$\left(\frac{dT_t}{du'}\right)_{r.,} = \frac{\chi'}{\rho' c'_p}\cdot\frac{1}{u'^2} = \frac{T_{:k} - T_:}{u'}. \qquad (5,\ 12)$$

Condition (5,10) is written thus:

$$\frac{T_{:k} - T_:}{u'} = \frac{2RT_:^2}{E}\frac{1}{u'}; \quad T_{:k} - T_: = \frac{c'_t}{c''_p}(T_k - T_0) = \frac{2RT_:^2}{E}\ \gamma\gamma$$

$$\cong \frac{2RT_{:k}^2}{E}; \quad T_k - T_0 \cong \frac{c''_p}{c'_p}\frac{2RT_{:k}^2}{E} \cong \frac{c''_p}{c'_p}\cdot\frac{2RT_{:k}T_:}{E}. \qquad (5,\ 13)$$

Substituting into (5,7), we find at the point of intersection

$$u_B' = u'(T_B) = \frac{1}{e}u'(T_{:k}). \qquad (5,\ 14)$$

The condition of the limit of steady-state combustion is related to the temperature dependence of the combustion rate. The last formula states that steady-state combustion is possible only at an initial temperature such that the combustion rate is no less than 1/e, i.e. no less than 37% of the combustion rate of the C phase, heated continuously to the temperature T_b. Above the limit, the dependence of the steady-state rate on the initial temperature undergoes no changes.

It is curious to compare the result with the theory of the limit of flame propagation in gases, developed by the author [15]. In the case of gases, the presence of a limit depends only on the heat removal to outside; combustion is possible only until the heat removal reduces the combustion rate no more than to $1/\sqrt{e}$, i.e. to 61% of the adiabatic rate. The essential difference lies in the extremely steep drop near the limit in the case of the gas. The principal difference lies in the fact that in the gas no steady-state solutions exist below the limit; in the case of combustion of the C phase considered here, steady-state systems exist -- theoretically -- but are unstable and hence unrealizable.

The result obtained is in agreement with the experimental findings. Thus, in A. F. Belyayev's experiments [9], at the boiling point of nitro-

glycol, $u'(T_{cb}) = 0.65$ mm/sec.* The lowest measured rate was 0.26 mm/sec at 0° (Andreyev), i.e. 40% of $u'(T_{cb})$. According to a personal communication of A. F. Belyayev, steady-state combustion could not be observed at a lower temperature.

K. K. Andreyev's article [14] contains much interesting material on this problem. Thus, according to his observations, nitroglycol does not give steady-state combustion at atmospheric pressure and room temperature. Steady-state combustion can be observed when the pressure is lowered to 230-380 mm, upon which the boiling point is reduced to 210-225°C instead of 245°C at 760 mm.

This example is especially convincing because when the pressure is lowered, the combustion temperature can only be lowered, and the combustion rate decreases appreciably. The heat losses to outside, by which the limit is usually explained, only increase; it is difficult to find another explanation of the observed fact.

The explanations advanced by K. K. Andreyev are qualitative in character and anticipate the more detailed representations developed here: thus, Andreyev writes of the necessity of preheating for the ignition of a condensed substance, of the possibility of quenching as a result of the dissipation within the substance of the heat that was concentrated in a thin layer at the surface, etc.

In the case of combustion of condensed substances, the investigation of nonsteady-state processes, considering the nonadiabatic character of combustion, which we do not present here, leads to the following conclusions:

1. At a given T_o and properties of the substance, the presence of heat removal to outside leads -- in the case of a small heat removal -- to a decrease in the velocity of the flame as against the adiabatic steady-state value, and -- in the case of a sufficiently great heat removal -- to the impossibility of combustion.

2. Under given external conditions (tube diameter, etc.), the relative heat removal, on which the rate and possibility of combustion depend, is greater, the lower the combustion rate; the existence of a limit of the possibility of combustion at low pressure, depending on the drop in combustion rate with decreasing pressure (together with the possibility of the existence of an upper limit, depending on the increase in T_b with increasing pressure -- see the example of nitroglycerin above) is thus natural.

3. The system of combustion at the limit (including the limit depending on the heat removal) lies at the boundary of stability of the steady-state system. The boundary of possibility of the steady-state system (see [15]) is not reached.

4. In the one-dimensional theory, the rate at the limit can be calculated as a function of the quantity characterizing the heat removal.

---

*The rate observed at 184° is 0.62 mm/sec. At a higher temperature the formation of bubbles hinders the measurement. The figure cited in the text was obtained by extrapolation to $T_b = 200°C$.

In all cases

$$\frac{u'(T_{_{\!A}})}{\sqrt{e}} > u'_{\text{прех}} > \frac{u_{_{\!A'}}}{\sqrt{e}} , \tag{5, 15}$$

where u'_{lim} is the rate at the limit, u_{ad} is the adiabatic steady-state combustion rate (calculated according to (5,3) without losses to outside).

In the light of the definite theoretical predictions, a detailed experimental investigation of the problem is desirable.

The condition of tangency found (5,14) is vital for the theory of ignition. The necessary condition for ignition consists of the fact that at a surface temperature T_b the gradient should be no greater than that which corresponds to tangency of the curves, φ_B. At point B, we find, according to (5,8) and (5,14)

$$\varphi_{_B} = \frac{c_p''\rho'}{\tau_{_1}'}(T_{_{\!A}} - T_{_B})u'_{_B} = \frac{\rho'c_p''}{\tau_{_1}'}\frac{2RT_{_{\!A}}^2}{E}\frac{u'(T_{_{\!A}})}{e} . \tag{5, 16}$$

The value of the gradient necessary for ignition does not depend on the temperature of the C phase, T_o; however, the amount of heat and duration of preheating necessary to reach $\varphi = \varphi_B$ at the surface do depend on T_o.

With accuracy within an order of magnitude, we find:

$$x_{_B} \approx \frac{T_{_{\!A}} - T_0}{\varphi_{_B}} \approx \frac{(T_{_{\!A}} - T_0)E}{2RT_{_{\!A}}^2} \cdot \frac{c_p'}{c_p''} \frac{\chi'e}{u'(T_{_{\!A}})} \tag{5, 17a}$$

$$t_{_B} \approx \frac{x_{_B}^2}{\chi'} = \left[\frac{(T_{_{\!A}} - T_0)E}{2RT_{_{\!A}}^2}\frac{c_p'}{c_p''}\right]^2 \frac{\chi'e^2}{[u'(T_{_{\!A}})]^2} \tag{5, 17b}$$

$$q_{_B} \approx \rho'c_p'(T_{_{\!A}} - T_0)x_{_B} \approx \frac{(T_{_{\!A}} - T_0)^2E}{2RT_{_{\!A}}^2}\frac{c_p'}{c_p''}\frac{\tau_{_1}'e}{u'(T_{_{\!A}})} , \tag{5, 17c}$$

where x_B is the width of the preheated layer,
t_B is the necessary time of preheating,
q_B is the amount of heat consumed for the preheating.
Let us mention that the condition for the possibility of steady-state combustion (5,13) can be written)

$$\frac{(T_{_{\!A}} - T_0)E}{2RT_{_{\!A}}^2}\frac{c_p'}{c_p''} \leqslant 1. \tag{5, 18}$$

Substituting into (5,17), we obtain the upper limit of the corresponding values (time of preheating and amount of heat necessary for ignition) at the lowest temperature at which combustion is possible. As the temperature T_o is increased, the amount of heat and time required for ignition decrease as $(T_b - T_o)^2$; the experimental results are in qualitative agreement with these conclusions. Let us mention that in addition to preheating of the C phase, ignition of the ES vapors formed is also

31

necessary for inflammation; the amount of heat consumed for this is extremely small in comparison with the heat consumption for preheating of the C phase (approximately in the ratio of the relaxation times -- see the beginning of the section).

We have presented above the problem of nonsteady-state combustion as applied to secondary explosives. As applied to smokeless powder, a possible complicating factor is its multicomponent nature; in connection with this, the fact of the steady-state combustion of nitroglycerin, gelatin'zed by 1% nitrocellulose, cited by Andreyev [14], is interesting. In the case of smoky powders and pipe compositions, the role of the condensed combustion products, adhering to the burning surface and accumulating heat, may be vital.

Finally, the considerations developed on the conditions of inflammation and the possibility of combustion can also be applied to the combustion of coal, liquid fuel, etc. at the expense of the oxygen of the surrounding medium. In these cases, the temperature gradient in the C phase (in coal or oil) also plays a role in the thermal balance; a whole series of vital differences, especially the different form of the combustion rate curve as a function of the parameters, makes a special consideration, not appropriate here, essential.

In addition to the problems of inflammation and the possibility (limit) of combustion, the concepts developed are essential for the combustion of ES or powder under variable conditions, in particular -- in the case of inconstant pressure. A variable combustion rate also corresponds to variable pressure; each value of the combustion rate has its own corresponding value of the gradient φ, established in the steady-state system; it is precisely at this value φ_s that the steady-state value of the combustion rate is realized. And yet, when the pressure is changed rapidly, the temperature distribution in the C phase does not have time to follow the pressure change; corresponding to the φ differing from the steady-state value, we should expect that the combustion rate will also differ from the steady-state value. When the pressure is changed rapidly, the combustion rate proves to depend not only on the instantaneous pressure, but also on the curve of its variation, which distorts the classical combustion law.

According to Yu. B. Khariton's observation, the considerations developed make it possible to explain the unique phenomenon of quenching of powder in the barrel of a weapon after the shell is ejected: at high pressure the combustion rate is great, the temperature gradient is great, and the preheated layer of powder is thin. The ejection of the shell is accompanied by a sharp pressure drop. The powder is capable of burning quite stably at atmospheric pressure, but its combustion occurs at a small -- comparatively -- rate, at small φ, and requires a substantial thickness of the preheated layer. Hence the heating of powder burning at high pressure can prove insufficient for inflammation at atmospheric pressure; when the pressure drops rapidly, the temperature distribution does not have time to readjust; the anomalously steep -- for combustion at low pressure -- temperature gradient leads to a lowered combustion temperature and to

32

extinguishment of the powder grains, in particular those that have remained in the barrel. It would be extremely interesting to analyze in detail the change in heat distribution in the powder in a problem of internal ballistics, in a manometric bomb, and in a weapon, and its influence on the combustion law.

In conclusion, let me express my sincere gratitude to my colleague at the Institute, A. F. Belyayev, O. I. Leypunskiy, D. A. Frank-Kamenetskiy, and Yu. B. Khariton for their interest in the work and their valuable comments, as well as for providing the possibility of discussion and the use of their unpublished results.

SUMMARY

1. A scheme of combustion of smokeless powder is proposed, providing for its conversion to energy-rich gaseous substances by heterogeneous reaction and the subsequent reaction of these substances, liberating the heat of combustion in the gaseous phase at the surface of the powder -- in analogy with A. F. Belyayev's scheme of the combustion of ES.

2. A theory of steady-state combustion of condensed substances (secondary ES and powders), determining the temperature distribution, concentration distribution, and combustion rate, was discussed.

3. A consideration of the exothermic reaction in the liquid phase leads to the impossibility of steady-state combustion at a high boiling point. When the limit is reached, the combustion turns into detonation. Formulas are given for calculating the conditions of transition.

4. A nonsteady-state theory of the combustion of condensed substances was constructed, based on the fact that the relaxation time of the heat distribution in the condensed phase is many times greater than the relaxation time of the gaseous phase.

5. A combustion limit, reached when the combustion rate drops to 37% of the combustion rate at the boiling point, was predicted on the basis of nonsteady-state theory. The limit depends on the internal instability of combustion, and not on external heat losses.

6. A theory of the ignition of condensed substances was constructed on the basis of nonsteady-state theory.

The time and amount of heat required for ignition are determined chiefly by the preheating of the condensed phase and are proportional to the square of the difference of the boiling point and the initial temperature.

BIBLIOGRAPHY

1. Belyayev A. F. _Zhurn. Fiz. Khimii_ (Journal of Physical Chemistry), 12, 93, 1938.
2. Zel'dovich Ya. B. and Frank-Kamenetskiy D. A. _Zhurn. Fiz. Khimii_, 12 100, 1938.

3. Belyayev A. F. DAN (Reports of the Academy of Sciences USSR), 24, 253, 1939.
4. Langmuir I. Journ. Amer. Chem. Soc., 54, 2806, 1932.
5. Hellund A. Phys. Rev., 57, 319, 328, 737, 743, 1940.
6. Lewis B. and Elbe G. Journ. Chem. Phys., 21, 537, 1934.
7. Frank-Kamenetskiy D. A. Zhurn. Fiz. Khimii, Vol. 13, 738, 1939.
8. Zel'dovich Ya. B. and Semenov N. N. ZhETF (Journal of Experimental and Theoretical Physics), 10, 1116, 1940.
9. Belyayev A. F. Zhurn. Fiz. Khimii, 14, 1009, 1940.
10. Muraour H. C. R., 187, 289, 1928; Bull. Soc. Chim., (4) 53, 613, 1933; cited in Muraour, Mém. Art., Franc., 17, 831, 1938.
11. Jamaga N. Zs. ges. Schiess Sprengstwesen, II, 1930; cited according to translation in Mém. Art. Franc., 10, 867.
12. Flamm P. and Mache H. Wiener Ber., 126, 9, 1917; Mache H. Die Physik der Verbrennungserscheinungen, Veita-Co, Leipzig, 1918.
13. Belyayev A. F. The Appearance of Detonation of Explosives under the Action of a Heat Pulse. Sbornik Statey po Teorii VV (Collection of Articles on the Theory of Explosives), edited by Andreyev and Khariton, State Publishing House of the Defense Industry, 1940, pp. 7-20.
14. Andreyev K. K. Experimental Investigation of the Combustion of Explosives. Sbornik Statey po Teorii VV, edited by Andreyev and Khariton, State Publishing House of the Defense Industry, 1940, p. 39, 60.
15. Zel'dovich Ya. B. ZhETF, 11, 159, 1941.

REPRODUCTION QUALITY NOTICE

This document is the best quality available. The copy furnished to DTIC contained pages that may have the following quality problems:

- Pages smaller or larger than normal.

- Pages with background color or light colored printing.

- Pages with small type or poor printing; and or

- Pages with continuous tone material or color photographs.

Due to various output media available these conditions may or may not cause poor legibility in the microfiche or hardcopy output you receive.

☐ If this block is checked, the copy furnished to DTIC contained pages with color printing, that when reproduced in Black and White, may change detail of the original copy.

END

DATE
FILMED

10   65